

Influence of Mg, Ag and Al substitutions on the magnetic excitations in the triangular-lattice antiferromagnet CuCrO_2

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Magnetic excitations in CuCrO_2 , $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$, $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$, and $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ have been studied by powder inelastic neutron scattering to elucidate the element substitution effects on the spin dynamics in the Heisenberg triangular-lattice antiferromagnet CuCrO_2 . The magnetic excitations in $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ consist of a dispersive component and a flat component. Though this feature is apparently similar to CuCrO_2 , the energy structure of the excitation spectrum shows some difference from that in CuCrO_2 . On the other hand, in $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ and $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ the flat components are much reduced, the low-energy parts of the excitation spectra become intense, and additional low-energy diffusive spin fluctuations are induced. We argued the origins of these changes in the magnetic excitations are ascribed to effects of the doped holes or change of the dimensionality in the magnetic correlations.

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I. INTRODUCTION

Two-dimensional (2D) triangular-lattice antiferromagnet is one of the simplest playgrounds of the geometrical frustration. If Heisenberg spins on the triangular-lattice layer are coupled by the nearest neighbor exchange interactions, the frustration is dissolved by forming a 120° spin ordering. However, the ground state becomes nontrivial when there exist finite inter-layer or longer-distance couplings. In other words, if we can control these extra parameters, we can possibly create some novel states. Such attempts have recently been conducted on one of the model materials of the triangular-lattice Heisenberg antiferromagnets CuCrO_2 . In this compound, triangular-lattice layers of magnetic Cr^{3+} ions ($3d^3$) with $S = 3/2$ are separated from each other by non-magnetic layers of Cu^+ ions ($3d^{10}$). With decreasing temperature (T), the Cr spins form the three-dimensional (3D) magnetic ordering due to finite inter-layer couplings. The magnetic structure is a proper screw structure whose wave vector is $(q, q, 0)$ with q being slightly smaller than the value of the 120° structure, $q = 1/3$.¹⁻³ Recently, it was found that element substitution can induce interesting magnetic and transport properties. For example, substitution of the intra-layer Cr ions with non-magnetic Mg ions ($\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$) slightly increases the transition temperature of the 3D magnetic ordering (T_N), and sharpens the magnetic transition. Since the promotion of the 3D magnetic ordering is followed by increase of the magnetization, appearance of the magnetoresistance, and drastic enhancement of the electric conductivity, it was interpreted as the effect of holes introduced by the substitution of Cr^{3+} ions by Mg^{2+}

ions.^{4,5} On the other hand, substitution of the inter-layer Cu^+ ions with Ag^+ ions ($4d^{10}$) ($\text{Cu}_{1-y}\text{Ag}_y\text{CrO}_2$) and that of intra-layer Cr^{3+} ions with non-magnetic Al^{3+} ions ($\text{CuCr}_{1-x}\text{Al}_x\text{O}_2$) make the 3D magnetic ordering unclear. In both the systems, T^3 dependence of the low-temperature magnetic specific heat (C_{mag}) of CuCrO_2 is replaced by the T^2 dependence as the substitution is progressed, indicating the development of the two-dimensionality in the magnetic correlations. Moreover, close investigations of the C_{mag} 's and corresponding entropies showed that development of some unconventional low-energy spin fluctuations.^{6,7}

With these findings, we can expect that the element substitutions also affect the spin dynamics. Elucidation of this change in the spin dynamics should be important information to understand the origin of the physical properties of the substituted compounds and an important clue to produce novel phenomena in geometrically frustrated magnets by the element substitution. Accordingly, we performed inelastic neutron scattering study on powder samples of Mg, Ag, and Al substituted CuCrO_2 in addition to CuCrO_2 to observe their magnetic excitations as functions of momentum and energy transfers. We found that a variety of the magnetic excitations are induced by different types of the element substitutions.

II. EXPERIMENTS

About 3 cm³ polycrystalline samples of CuCrO_2 , $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$, $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$, and $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ were synthesized by a standard solid-state reaction method.⁴⁻⁷ They have rhombohe-

dral crystal structures (space group $R\bar{3}m$) with the lattice constants $a \sim 3.0$ Å and $c \sim 17$ Å. Their T_N 's determined by specific heat measurements are 24 K (CuCrO_2), 13 K [$\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$], 26 K [$\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$] and 24 K [$\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$].⁷ The neutron scattering measurements were performed with the time-of-flight technique using the cold neutron disk-chopper spectrometer AMATERAS at the Materials and Life Science Experimental Facility (MLF) in the Japan Proton Accelerator Research Complex (J-PARC).⁸ The power of the accelerator was ~ 120 kW. We utilized multiple incident energies of neutrons, $E_i = 15, 7.7, 4.7$, and 3.1 meV, which were produced simultaneously taking advantage of the repetition rate multiplication by the monochromating disk chopper.⁹ We analyzed all the data with the software suite UTSUSEMI¹⁰ to obtain the powder averaged scattering function $S(Q, E)$ (Q is the amplitude of momentum transfer and E is the energy transfer) as described in Ref. 11. The difference in utilized neutron flux between data was normalized versus the proton beam current incident on the neutron target. The difference in volume between the samples was normalized by intensities of nuclear Bragg peaks [CuCrO_2 and $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$] or the mole numbers [CuCrO_2 , $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ and $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$]. The preliminary results of the present study have been reported in Ref. 12.

III. RESULTS

A. CuCrO_2 and $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$

First, we show results for the two compounds which show clear 3D ordering behavior, CuCrO_2 and $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$. Figure 1(a) shows the $S(Q, E)$ map of CuCrO_2 measured at $T \sim 5$ K. It shows well defined magnetic excitations in particular around $Q = 1.4$ Å⁻¹, whose value corresponds to the wave vector of the magnetic ordering $\mathbf{Q}_m \sim (1/3, 1/3, 0)$. The magnetic excitations in CuCrO_2 consist of two kinds of components: one is a steep dispersive component at $Q_m \sim 1.4$ Å⁻¹. The other is a less dispersive component (flat component) at $E \sim 5$ meV spreading over a wide range of Q .¹¹ By comparing our data with the magnetic excitation spectra for single crystal samples,^{13,14} the dispersive component and the flat component correspond to the α and β modes in Ref. 13, respectively. The flat component forms a large peak at $E \sim 5$ meV in the energy profile as shown by closed circles in Fig. 2, and the dispersive component shows a tail at lower energies whose intensity decreases with decreasing the energy. In addition, there exist weak but finite excitations at a higher-energy region than the flat component, as manifested by diffusive signal around 10 meV in Fig. 1(a) and a tail in the energy profile in Fig. 2. They may correspond to the β' mode in Ref. 13.

$\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ shows apparently similar excitation spectrum to that of CuCrO_2 : It consists of a dispersive

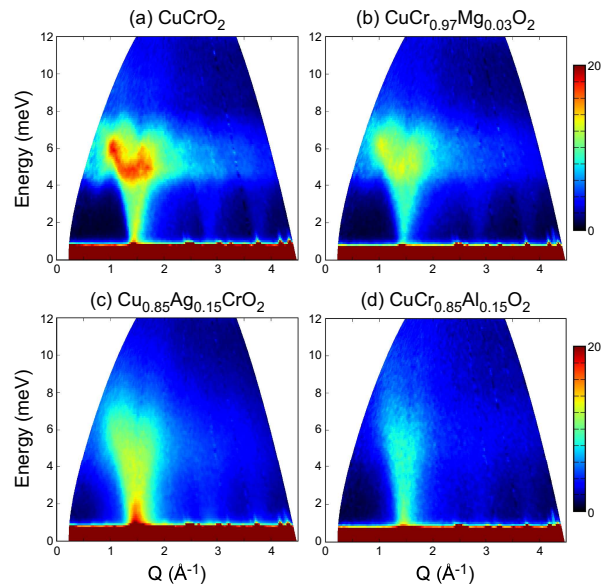


FIG. 1. (Color online) Q - E maps of the excitation spectra of (a) CuCrO_2 , (b) $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$, (c) $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$, and (d) $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ measured at 6, 5, 5 and 4 K, respectively, with $E_i = 15$ meV.

component and a substantial flat component [Fig. 1(b)], and its energy profile shows a large peak at $E \sim 5$ meV (open circles in Fig. 2). However, the overall weight of the excitation spectrum of $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ is smaller than that of CuCrO_2 . The reduction of the spectral weight may partly be attributed to disorder introduced by the Mg substitution, which was confirmed by recent μSR ¹⁵ and thermal conductivity studies¹⁶. However, we found that the reduction in spectral weight depends on energy, and it is especially evident around the peak at $E \sim 5$ meV as well as in a low-energy part of the spectrum at $E < 4$ meV. Though the reduction at these energies is particularly evident in the energy profile around $Q_m \sim 1.4$ Å⁻¹ [Fig. 2(a)], it remains even if we integrate the excitation spectra over as wide a Q region as possible [Fig. 2(b)]. This means that the reduction of the spectral weight cannot be explained only by the broadening in Q by the disorder. In fact, the Q profile of the low-energy part of the excitation spectra in $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ has almost similar width to that in CuCrO_2 [Fig. 5(a)]. On the other hand, $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ has a higher weight in a higher-energy region (at $E \sim 8$ meV). These facts show that the Mg substitution does not only induces reduction of the spectral weight but also induces a change of the energy structure of the magnetic excitations.

The similarity in the slope of the dispersive component between CuCrO_2 and $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ [Figs. 1(a) and 1(b)] suggests that the exchange interactions between the nearest Cr sites, J_1 , is almost the same in the both compounds. On the other hand, the difference in the weight of the flat component suggests that there is some difference in the exchange interactions between the second nearest neighbor Cr sites, J_2 , since

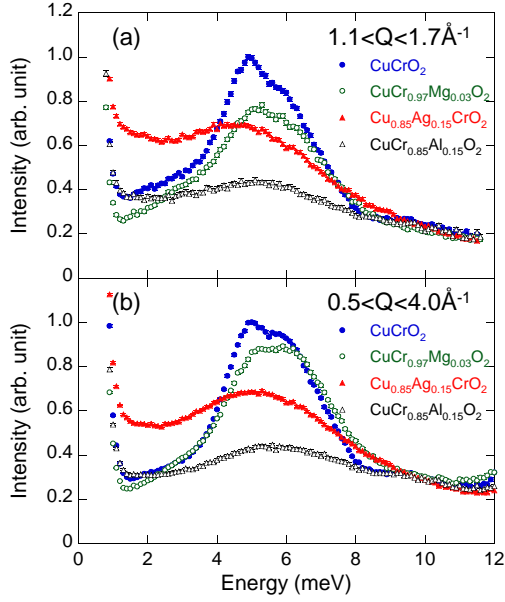


FIG. 2. (Color online) Energy dependence of the excitation spectra of CuCrO_2 (closed circles), $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ (open circles), $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ (closed triangles), and $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ (open triangles) measured at 6, 5, 5 and 4 K, respectively, with $E_i = 15$ meV. The data are obtained by integrating the data shown in Fig. 1 over Q ranges of (a) $1.1\text{--}1.7 \text{ \AA}^{-1}$ and (b) $0.5\text{--}4.0 \text{ \AA}^{-1}$. The vertical axes are scaled so that peaks of the CuCrO_2 data at $E \sim 5$ meV become unity.

the energy of the flat mode (β mode) is determined by J_2 .¹³ This argument of J_1 and J_2 is also supported by the magnetic excitations at $T > T_N$. Since the magnetic correlations start to develop far above T_N for the both compounds,^{1,4,17} they show clear magnetic excitations at $Q \sim 1.4 \text{ \AA}^{-1}$ at $T > T_N$.¹¹ Figure 3 shows the dynamical susceptibility $\chi''(Q, E) = S(Q, E)/[1 - \exp(-E/k_B T)]$ at $Q = 1.4 \text{ \AA}^{-1}$, which are derived from constant- Q cuts of $S(Q, E)$ at 60 K and 30 K. At 60 K, far above T_N , the shapes of χ'' 's of the both compounds completely coincides with each other [Fig. 3(a)]. However, at 30 K, slightly above T_N , the peak position of χ'' of CuCrO_2 decreases with approaching the critical divergence, while that of $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ stays at almost the same energy as 60 K [Fig. 3(b)]. This difference in the temperature dependence of χ'' is consistent with a recent electron spin resonance (ESR) study.¹⁷ They reported that the ESR intensity of CuCrO_2 drops rapidly below 50 K, while that of $\text{CuCr}_{0.98}\text{Mg}_{0.02}\text{O}_2$ shows a monotonous increase with cooling and reduces rapidly only below T_N . The small temperature dependence of χ'' of $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ observed in the present study should be related to the monotonous increase of the ESR intensity at $T > T_N$ in Ref. 17. Considering that the peak energy in χ'' (arrows in Fig. 3) is a measure of the energy scale of spin fluctuations, the difference in the temperature dependence of χ'' may be attributed to

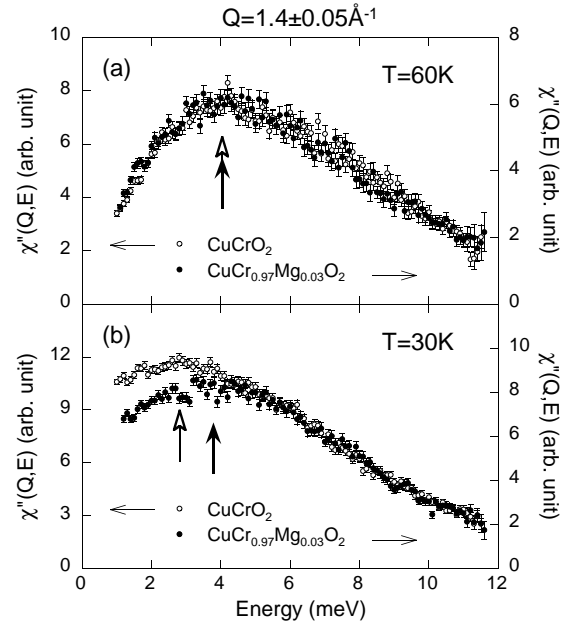


FIG. 3. $\chi''(Q, E)$ of CuCrO_2 (open circles) and $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ (closed circles) at $Q = 1.4 \pm 0.05 \text{ \AA}^{-1}$ measured at (a) 60 K and (b) 30 K, which are deduced from data with $E_i = 15$ meV. White and black arrows indicate the peak positions in $\chi''(Q, E)$ of CuCrO_2 and $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$, respectively.

some difference in the magnetic interactions between the two compounds. Since the contribution of the largest magnetic exchange interaction J_1 to the magnetic excitation spectrum becomes dominant at high temperatures, the almost identical χ'' 's for the two compounds at 60 K suggest that J_1 's in CuCrO_2 and $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ have almost the same values. On the other hand, the contribution of longer-distance interactions J_2 etc. with smaller magnitudes become effective with decreasing temperature. Therefore, the difference in χ'' at 30 K suggests the difference in J_2 or longer-distance interactions between the two compounds.

In order to see the difference in low-energy part of the excitations in more detail, we investigated the data with a lower $E_i = 4.7$ meV at $T \sim 5$ K. The $S(Q, E)$ map of CuCrO_2 shows a sharp ridge in a broader dispersive excitations with a tail in the higher Q side [Fig. 4(a)]. This feature indicates that there exist clear spin wave excitations, but the inter-layer coupling is much smaller than the intra-layer coupling.¹⁸ By looking at the excitation spectra carefully, we found that there is a discontinuity in the ridge excitations around 1 meV. This feature can be seen more clearly in the energy profile shown by closed circles in Fig. 5(a), where there are shoulders around $E = 0.5$ meV and 1.5 meV. The former should be attributed to the spin gap which was reported by the previous single crystal study.¹³ On the other hand, the existence of the shoulder at $E = 1.5$ meV suggests that there is the second gap in the spin wave dispersion in

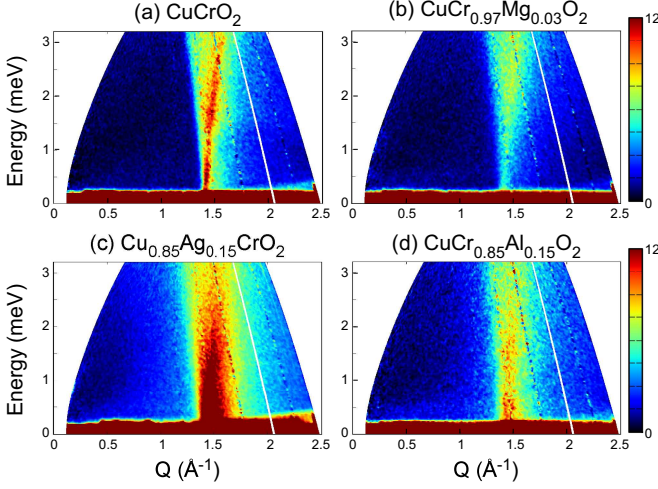


FIG. 4. (Color online) Q - E maps of the excitation spectra of (a) CuCrO_2 , (b) $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$, (c) $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$, and (d) $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ measured at 6, 5, 5 and 4 K, respectively, with $E_i = 4.7$ meV.

CuCrO_2 around the zone center. Very recently, we confirmed that the gap at $E = 1.5$ meV in our preliminary single crystal study. The two gaps indicate there are two kinds of single ion anisotropies in CuCrO_2 , which may be ascribed to the easy-axis anisotropy along the z axis and the easy-plane anisotropy in the spiral plane.¹³

On the other hand, in $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ the spectral weight decreases faster than that in CuCrO_2 with decreasing the energy [Figs 4(b) and 5(a)]. This energy dependence is quite interesting considering that generally the structure factor of antiferromagnetic spin wave is proportional to $1/E$. Another interesting feature in the spectrum of $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ in contrast to CuCrO_2 is that there is no gap or shoulder structure. These results indicate that the Mg substitution induces a change in the single-ion anisotropies in addition to the energy structure of the excitation spectra.

B. $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ and $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$

Next, we show results for the rest of the samples, $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ and $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$, where 3D magnetic transition becomes suppressed and 2D character becomes evident in the specific heats. In $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ [Fig. 1(c)], the dispersive component becomes diffusive even at temperature far below T_N , and the weight of the excitation spectrum shifts to a lower energy. Moreover, the flat component decreases its intensity and is hard to observe. As a result, the low-energy part ($E \lesssim 4$ meV) of the excitations has similar spectral weight to those at $E \sim 5$ meV with a steep increase below $E \lesssim 2$ meV (closed triangles in Fig. 2). These features should be associated with the increase of the two dimensionality in the magnetic excitations.¹¹

The excitation spectrum of $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ looks

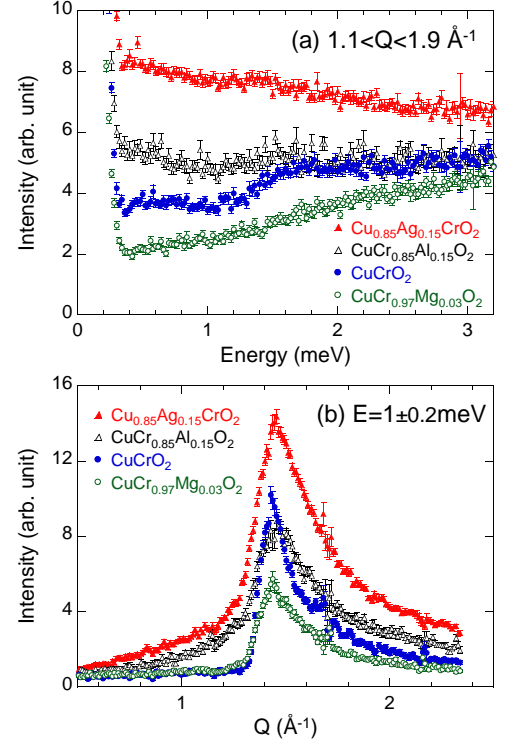


FIG. 5. (Color online) (a) Energy dependence of the excitation spectra obtained by integrating the data in Fig. 4 over Q ranges of 1.1 – 1.9 \AA^{-1} . (b) Constant- E cuts of the data in Fig. 4 at $E_i = 1$ meV with a width of ± 0.2 meV. Closed circles, open circles, closed triangles, and open triangles show data of CuCrO_2 , $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$, $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$, and $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$, respectively.

similar to $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ in that it consists of a diffusive dispersive component and a very weak flat component [Fig. 1(d) and open triangles in Fig. 2]. This fact suggests that the spin dilution in the Cr layers introduce a similar effect in the magnetic correlations to that introduced by decrease in the inter-layer coupling by the Ag substitution. However, $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ has much smaller spectral weight than $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$. The ratio of the spectral weight between $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ and $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ is independent on the Q region over which the data are integrated [Figs. 2(a) and 2(b)]. This means the low spectral weight in $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ is not caused by broadening of the spectrum in Q . Of course, it is partly explained by the 15% dilution of Cr spins by the Al substitution. However, the difference between the two compounds is much larger than 15%: the intensity of $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ is about 60% of that of $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ at $E \lesssim 5$ meV. The large reduction of the spin fluctuations may be related to the spin-glass-like behavior observed in $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$.⁷ We should also note that the excitation spectrum of $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ [Fig. 1(d)] is completely different from that of $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$, which is another evidence that the difference in the magnetic excitations between

$\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ and CuCrO_2 can not be explained only by the spin dilution effect.

Figures 4(c) and 4(d) show low-energy parts of excitation spectra of $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ and $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ around $Q = Q_m$ measured with $E_i = 4.7$ meV. Their energy dependences obtained by integrating the data over Q are shown in Fig. 5(a). The spectral weight of $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ monotonically increases as the energy decreases [Fig. 4(c) and closed triangles in Fig. 5(a)]. The spectral weight of $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ also shows increase as the energy decreases, though its intensity is lower than that of $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ [Fig. 4(d) and open triangles in Fig. 5(a)]. The resemblance in the low-energy spectra of the two compounds is also found in their Q dependences. Figure 5(b) shows Q profiles of the excitation spectra of the four compounds at $E = 1$ meV. In CuCrO_2 , the profile shows a sharp rise at $Q < Q_m$ and gradual decrease at $Q > Q_m$, forming a single skewed peak with a long tail at a higher Q region. $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ also shows a similar single skewed profile, though its intensity is about half of that of CuCrO_2 . In contrast to these compound which form clear 3D magnetic orderings, Q profiles of $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ and $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ consist of two components: one is a broad component with less intensity and long tails even at $Q < Q_m$, and the other is a sharper component like CuCrO_2 . As discussed in Ref. 11, the broad components manifest the existence of diffusive low-energy spin fluctuations in addition to disordered spin waves, and they are attributed to the origin of the AT^2 term in the low-temperature C_{mag} with a large value of A .

IV. DISCUSSION

The present study revealed that the Mg substitution induces very different features in the magnetic excitation spectrum from the Ag and Al substitutions. While the Mg substitution preserves the sharp dispersive component at low energies at $Q \sim Q_m$ and flat component at $E \sim 5$ meV like CuCrO_2 , the Ag and Al substitutions reduce the flat component and make the low-energy part of the excitation spectra diffusive and intense. These difference must be related to the difference in the dimensionality of the magnetic ordering, which has been confirmed by the specific heat measurements.^{6,7}

Although the magnetic excitations in CuCrO_2 and $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ has the above mentioned similarities, there are clear differences in the excitation spectrum between $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ and CuCrO_2 . The Mg substitution reduces the spectral weight in particular at low energies and around the flat component ($E \sim 5$ meV), while it increases a high-energy part ($E \sim 8$ meV) of the spectrum. There is also difference in temperature dependence of the magnetic excitations in the paramagnetic phase. In addition, the two kinds of spin gaps at $Q = Q_m$ disappear. These facts indicate that the Mg substitution affects the magnetic exchange interac-

tions, in particular longer-distance interactions than J_1 , as well as the single-ion anisotropies. They may cause the slightly higher T_N and the sharper magnetic transition in $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ than in CuCrO_2 .

Though the 3% spin dilution may induce some disorder in the magnetic correlations,^{15,16} it alone cannot explain these changes, which is also supported by the fact that the spin dilution by the Al substitution induces completely different effects in the magnetic excitations. One of the plausible origins of the above changes in the magnetic excitations is a change in the crystal structure induced by the 3% substitution of Mg, where the lattice constants show 0.2–0.3% increase.⁴ However, the increase of the lattice constants should decrease the antiferromagnetic exchange interactions,¹⁹ which is inconsistent with the slight increase of T_N by the Mg substitution,⁵ and suggests that the change in the crystal structure has little effect on the magnetic exchange interactions. On the other hand, the Mg substitution increases the magnetization and induces negative magnetoresistance effect, which were attributed to a coupling between doped holes and the Cr spins.⁴ Then, a more interesting scenario is that the holes introduced by the Mg substitution and concomitant increase in the electron conductivity modify the magnetic excitations. One of the plausible scenarios of the coupling between the holes and the Cr spins is that ferromagnetic exchange interactions due to the double-exchange interactions. They can modify the magnetic excitations over long distances through the hopping of holes, and this scenario is consistent with the increase of the magnetization. However, it is still inconsistent with the increase of T_N , because the ferromagnetic fluctuations should compete with the antiferromagnetic exchange interactions and lower T_N . Okuda *et al.* proposed the stabilization of the magnetic ordering by the order-by-disorder mechanism to reconcile the ferromagnetic fluctuations and the increase of T_N .^{5,16} Another interesting scenario related to the doped holes is the orbital degree of freedom. Since CrO_6 octahedra of CuCrO_2 are compressed along the c axis, t_{2g} orbitals of a Cr ion split into a doubly degenerate states with a higher energy and a non-degenerate state with a lower energy by the crystal electric field. In CuCrO_2 , there are three electrons in t_{2g} orbitals of Cr^{3+} ions, which results in no orbital degree of freedom. However, in $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$, doped holes which enter the doubly degenerate orbitals can produce the orbital degree of freedom. Therefore, it is plausible that hopping of the holes induces change of the single-ion anisotropies as well as exchange interactions between spins through the change of the orbital states. Though whether this scenario can mainly affect longer-distance exchange interactions instead of J_1 is not clear, it might be possible depending on the orbital state.

On the other hand, the magnetic excitations of $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ are very similar to those of $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ except that their intensity is smaller than those of $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ by about 60%. This fact suggests that the both types of the element sub-

stitutions induce similar effects on the magnetic excitations. In particular, the appearance of additional diffusive low-energy fluctuations is interesting with expectations for unconventional spin fluctuations such as spin liquid^{20,21} or Z_2 vortex.^{22,23} In our previous neutron scattering study on $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$, we interpreted this low-energy spin fluctuation as the origin of the large T^2 component of C_{mag} .¹¹ In this study, $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ also shows this diffusive low-energy fluctuation, which is consistent to the fact that $\text{CuCr}_{1-x}\text{Al}_x\text{O}_2$ also has the T^2 components in its C_{mag} .⁷ In $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$, the change in the magnetic excitations should be attributed to the enhancement of the two-dimensionality by the substitution of the inter-layer Cu ions by Ag ions. In contrast, the direct effect of the Al substitution is to disturb the magnetic correlations in the Cr layers. However, since the 3D ordering of a quasi-2D system depends on the development of the intra-layer correlations in a mean-field approximation,²⁴ the Al substitution can indirectly weaken the magnetic correlations between the layers, thereby inducing similar effect on the magnetic excitations as the Ag substitution.

V. CONCLUSION

We studied magnetic excitations in CuCrO_2 , $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$, $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$, and $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ by inelastic neutron scattering to elucidate the element substitution effects on the spin dynamics in the triangular-lattice antiferromagnet

CuCrO_2 . We found that the magnetic excitations in CuCrO_2 and $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ consist of sharp dispersive components at low energies at $Q \sim Q_m$ and the flat components at $E \sim 5$ meV, while in $\text{Cu}_{0.85}\text{Ag}_{0.15}\text{CrO}_2$ and $\text{CuCr}_{0.85}\text{Al}_{0.15}\text{O}_2$ the former components are diffusive and intense, and the latter components are much reduced. These difference must be related to the difference in the character of the dimensionality of the magnetic correlations. Furthermore, the Mg substitution changes the energy structure of the excitation spectrum, which suggests some modifications in the magnetic exchange interactions and single-ion anisotropies by the doped holes. The Ag and Al substitutions induce additional low-energy diffusive spin fluctuations, which are likely unconventional spin dynamics. The present results should be good examples how we can control the spin dynamics in triangular-lattice antiferromagnets by the element substitution, and give a hint to find a novel phenomenon in frustrated low-dimensional systems.

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